

TITLE OF THE INVENTION

Alicyclic Methacrylate Having
Oxygen Substituent Group on α -Methyl

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This invention relates to novel alicyclic methacrylate compounds having an oxygen substituent group on their α -methyl group which are useful as monomers for 10 polymerization to form base resins for use in micropatterning resist compositions.

BACKGROUND OF THE INVENTION

While a number of recent efforts are being made to 15 achieve a finer pattern rule in the drive for higher integration and operating speeds in LSI devices, deep-ultraviolet lithography is thought to hold particular promise as the next generation in microfabrication technology. In particular, photolithography using a KrF or ArF excimer 20 laser as the light source is strongly desired to reach the practical level as the micropatterning technique capable of achieving a feature size of 0.3 μm or less.

The resist materials for use in photolithography using light of an excimer laser, especially ArF excimer laser 25 having a wavelength of 193 nm, are, of course, required to have a high transparency to light of that wavelength. In addition, they are required to have an etching resistance sufficient to allow for film thickness reduction, a high sensitivity sufficient to eliminate any extra burden on the 30 expensive optical material, and especially, a high resolution sufficient to form a precise micropattern. To meet these requirements, it is crucial to develop a base resin having a high transparency, rigidity and reactivity. None of the currently available polymers satisfy all of these 35 requirements. There exists a strong demand to further improve resist materials.

Most common among high transparency resins used in the art are copolymers of acrylic or methacrylic acid derivatives. Active research works have been made on these copolymers to use them effectively as resist material. JP-A 4-39665 5 describes that an alicyclic structure such as adamantyl must be introduced as an ester substituent group into copolymers of acrylic or methacrylic acid derivatives in order to enhance the structural rigidity of the backbone and to provide necessary etching resistance. The introduction of an 10 alicyclic structure, on the other hand, increases the water repellency of polymers, which disturbs smooth development with an aqueous tetramethylammonium hydroxide solution, a developer, tending to have deleterious effects of forming micro-patterns with configuration defects and eventually 15 incurring pattern disruption. When these polymers are formulated as the base resin into resist compositions, the resulting resist compositions in some cases have satisfactory resolution, but do not withstand etching, and in other cases, have acceptable etch resistance, but a low resolution and 20 insufficient performance.

SUMMARY OF THE INVENTION

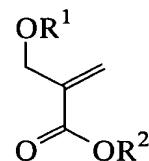
An object of the invention is to provide a novel alicyclic methacrylate compound having an oxygen 25 substituent group on its α -methyl group which is useful as a monomer for polymerization to form a base resin for use in a micropatterning resist composition which is improved in both etching resistance and resolution when processed by photolithography using light with a wavelength of up to 300 30 nm, especially ArF excimer laser light as the light source.

It has been found that alicyclic methacrylate compounds having an oxygen substituent group on their α -methyl group, represented by the general formulae (1), (2) and (3) below, are readily synthesized in high yields, that 35 polymers obtained through polymerization of these alicyclic methacrylate compounds having an oxygen substituent group on

their α -methyl group have high transparency at the exposure wavelength of an excimer laser, and that resist compositions using the polymers as the base resin have improved etching resistance and resolution upon lithographic processing.

5 Though not bound to the theory, it is believed that the alicyclic moiety in the inventive compounds largely contributes to the enhancement of etching resistance. With respect to the improvement in resolution, it is believed that the presence of an oxymethyl group in the inventive compounds 10 increases the hydrophilicity in proximity to the polymer backbone, enabling more smooth development.

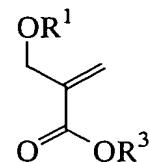
In a first aspect, the invention provides an alicyclic methacrylate having an oxygen substituent group on its α -methyl group, represented by the general formula (1).



(1)

15 Herein R^1 is hydrogen or an alkyl group of 1 to 10 carbon atoms which may contain a halogen atom, hydroxyl group, ether bond, carbonyl group, carboxyl group or cyano group, and R^2 is a monovalent organic group of 3 to 20 carbon atoms having 20 an alicyclic structure.

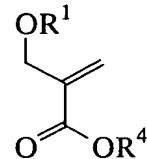
In a second aspect, the invention provides an alicyclic methacrylate having an oxygen substituent group on its α -methyl group, represented by the general formula (2).



(2)

Herein R¹ is as defined above, and R³ is a tertiary alkyl group of 4 to 20 carbon atoms having an alicyclic structure.

In a third aspect, the invention provides an alicyclic methacrylate having an oxygen substituent group on its 5 α-methyl group, represented by the general formula (3).



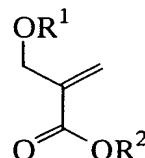
(3)

Herein R¹ is as defined above, and R⁴ is an organic group of 4 to 20 carbon atoms having a lactone structure.

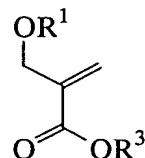
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DESCRIPTION OF THE PREFERRED EMBODIMENT

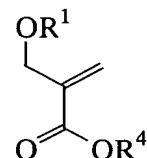
The alicyclic methacrylate compounds having an oxygen substituent group on their α-methyl group of the present invention have the general formulae (1), (2) and (3).



(1)



(2)



(3)

15 Herein, R¹ is hydrogen or an alkyl group of 1 to 10 carbon atoms which may contain a halogen atom, hydroxyl group, ether bond, carbonyl group, carboxyl group or cyano group. R² is a monovalent organic group of 3 to 20 carbon atoms having an alicyclic structure. R³ is a tertiary alkyl group of 4 to 20 20 carbon atoms having an alicyclic structure. R⁴ is an organic group of 4 to 20 carbon atoms having a lactone structure.

The C₁-C₁₀ alkyl group represented by R¹ may be either straight, branched or cyclic and contain a halogen atom, hydroxyl group, ether bond, carbonyl group, carboxyl group or

cyano group. Suitable alkyl groups are illustrated by methyl, ethyl, propyl, 2-propyl, butyl, 2-butyl, isobutyl, t-butyl, pentyl, hexyl, cyclohexyl, decyl, chloromethyl, dichloromethyl, trichloromethyl, trifluoromethyl,
5 2-hydroxyethyl, 2-hydroxypropyl, methoxymethyl, ethoxymethyl, 2-methoxyethoxymethyl, 1-ethoxyethyl, 2-tetrahydropyranyl, formyl, acetyl, methoxyacetyl, acetoxyacetyl, cyanomethyl, and 2-cyanoethyl.

Examples of the monovalent C₃-C₂₀ organic group having an alicyclic structure represented by R² include cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, dicycloheptyl, dicyclooctyl, dicyclononyl, dicyclodecanyl, tricyclodecanyl, adamantyl, tetracyclododecanyl, cyclohexylmethyl, dicycloheptylmethyl, isobornyl, menthyl,
10 hydroxycyclohexyl, hydroxydicycloheptyl, and hydroxyadamantyl as well as those groups illustrated for R³ and R⁴ later.

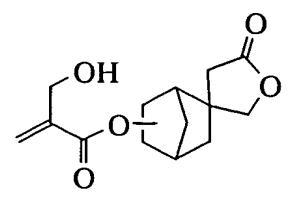
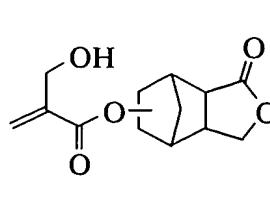
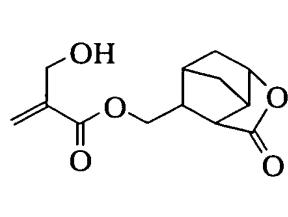
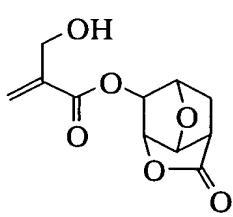
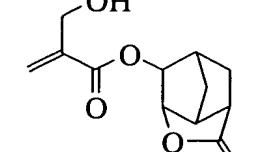
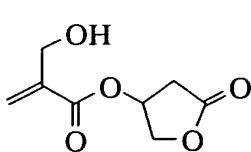
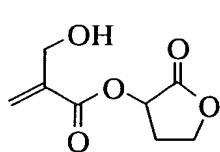
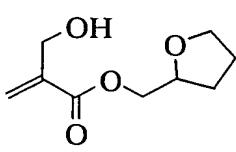
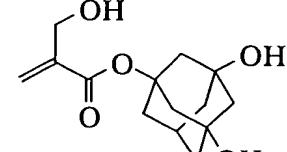
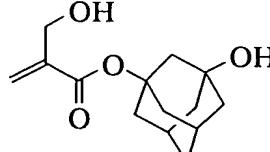
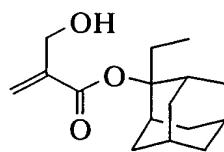
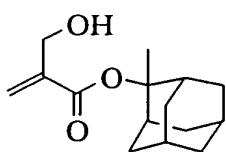
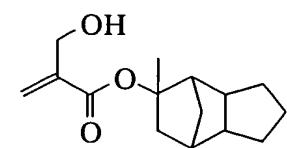
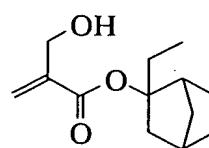
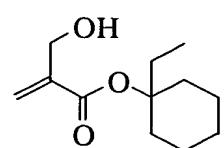
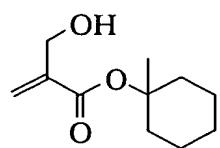
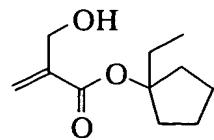
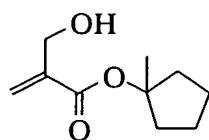
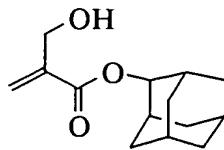
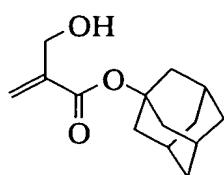
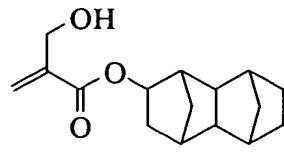
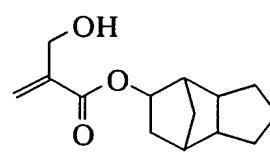
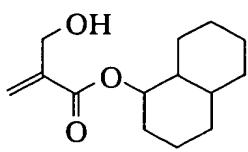
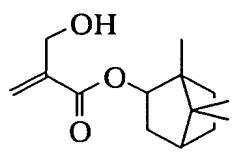
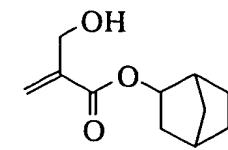
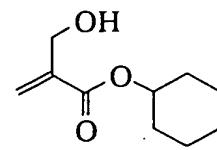
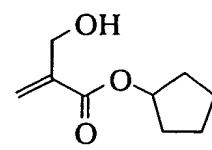
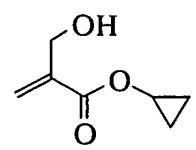
Examples of the C₄-C₂₀ tertiary alkyl group having an alicyclic structure represented by R³ include 1-methylcyclopropyl, 1-methylcyclopentyl, 1-ethylcyclopentyl,
20 1-methylcyclohexyl, 1-ethylcyclohexyl, 1-cyclopentylcyclopentyl, 1-cyclohexylcyclopentyl, 1-cyclopentylcyclohexyl, 1-cyclohexylcyclohexyl, 2-methyl-2-norbornyl, 2-ethyl-2-norbornyl, 8-methyl-8-tricyclo[5.2.1.0^{2,6}]decyl,
25 8-ethyl-8-tricyclo[5.2.1.0^{2,6}]decyl, 3-methyl-3-tetracyclo[4.4.0.1^{2,5},1^{7,10}]dodecyl, 3-ethyl-3-tetracyclo[4.4.0.1^{2,5},1^{7,10}]dodecyl, 2-methyl-2-adamantyl, 2-ethyl-2-adamantyl, 1-adamantyl-1-methylethyl, 1-methyl-3-oxo-1-cyclohexyl,
30 1-methyl-1-(tetrahydrofuran-2-yl)ethyl, 5-hydroxy-2-methyl-2-adamantyl, and 5-hydroxy-2-ethyl-2-adamantyl.

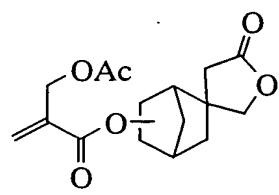
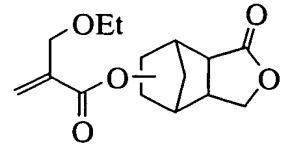
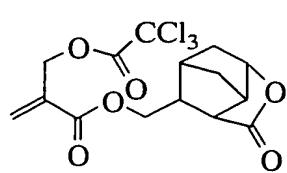
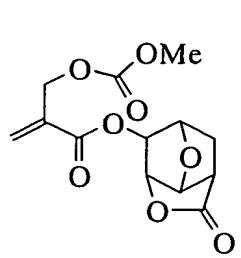
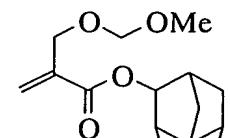
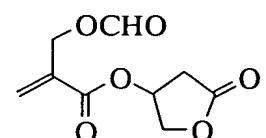
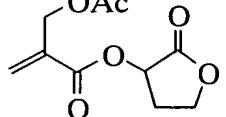
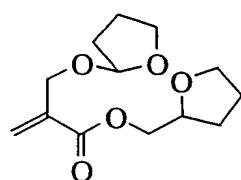
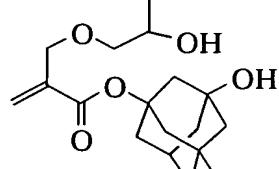
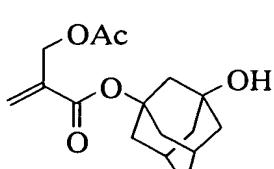
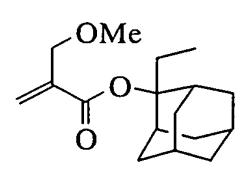
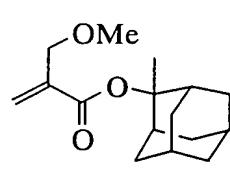
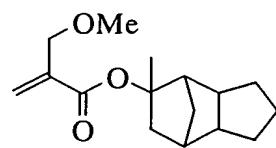
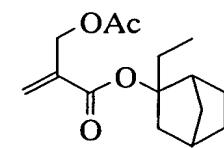
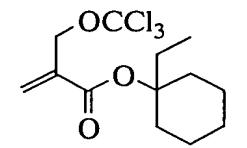
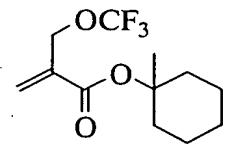
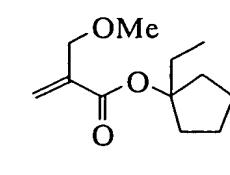
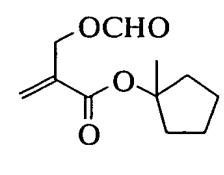
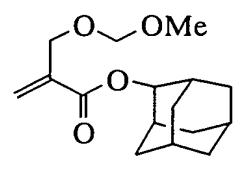
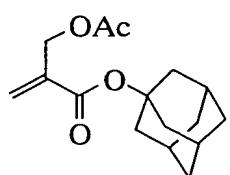
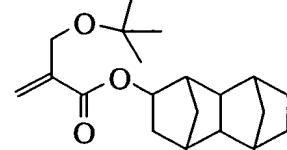
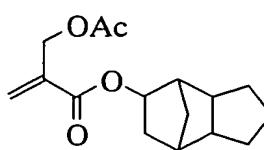
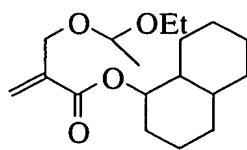
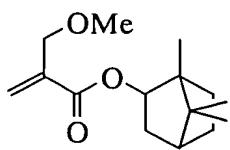
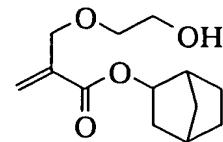
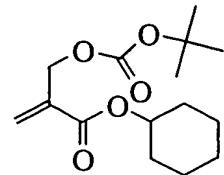
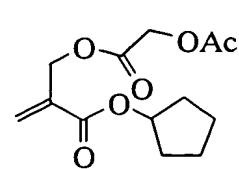
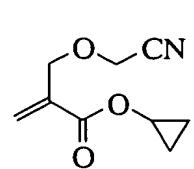
Examples of the C₄-C₂₀ organic group having a lactone structure represented by R⁴ include butyrolactonyl,
35 valerolactonyl, 1,3-cyclohexanecarbolactonyl, 4-oxa-5-oxotricyclo[5.2.1.0^{2,6}]decyl, 2,6-norbornanecarbolacton-3-ylmethyl,

2,6-norbornanecarbolacton-5-yl,
3-methoxycarbonyl-2,6-norbornanecarbolacton-5-yl, and
7-oxa-2,6-norbornanecarbolacton-5-yl.

By properly choosing R¹ and R², R³ or R⁴ in accordance
5 with a particular application, it is possible to optimize the
polarity and other properties of an overall molecule and
eventually, the characteristics of a photoresist utilizing
the inventive compound.

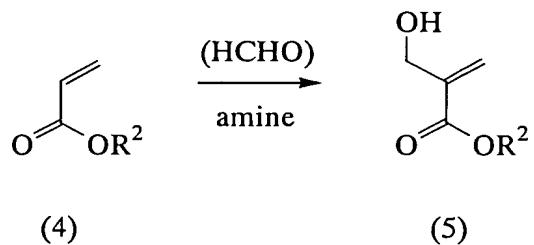
Illustrative, non-limiting, examples of the ester
10 compounds of the invention are given below. In the following
formulae, Me is methyl, Ac is acetyl and Et is ethyl.





The alicyclic methacrylate compound having an oxygen substituent group on the α -methyl group, represented by the formula (1), according to the present invention can be prepared, for example, by the synthesis process described below. In the practice of the invention, the synthesis process is not limited thereto.

Reference is first made to the compound of formula (1) wherein R¹ = H. It can be synthesized, as shown by the reaction scheme below, in one step from a corresponding acrylate compound of formula (4) which has been prepared by a routine process. This reaction is a hydroxymethylation of the acrylate compound at the α -position as shown below. One molar equivalent of a formaldehyde equivalent reacts on the acrylate compound of formula (4) in a solvent or solventless system in the presence of an amine compound to form an α -(hydroxymethyl)acrylate compound of formula (5).



Herein R² is a monovalent C₃-C₂₀ organic group having an alicyclic structure.

20 The amine compound used in the hydroxymethylation is
illustrated by trimethylamine, triethylamine, tributylamine,
pyridine, 4-dimethylaminopyridine,
1,4-diazabicyclo[2.2.2]octane, 1,5-diazabicyclo[4.3.0]non-5-
ene, and 1,8-diazabicyclo[5.4.0]undec-7-ene. An appropriate
25 amount of the amine compound used is 0.001 to 10 moles,
especially 0.01 to 1 mole per mole of the starting reactant.
With less than 0.001 mole of the amine, the reaction may not
proceed. More than 10 moles of the amine is wasteful because
no further effect corresponding to such an excess may be
30 exerted.

The formaldehyde equivalent is illustrated by gaseous formaldehyde, formalin, paraformaldehyde and 1,3,5-trioxane. An appropriate amount of the formaldehyde equivalent used is 0.2 to 10 moles, especially 0.5 to 2 moles of formaldehyde per mole of the starting reactant. With less than 0.2 mole of formaldehyde, a large portion of the starting reactant, acrylate compound may be left, leading to very low yields. More than 10 moles of formaldehyde can form a large amount of by-product, also leading to very low yields.

Examples of the solvent, if used in the hydroxymethylation, include hydrocarbons such as toluene, hexane and heptane; ethers such as dibutyl ether, diethylene glycol diethyl ether and tetrahydrofuran; alcohols such as methanol and ethanol; halogenated hydrocarbons such as 15 methylene chloride; esters such as ethyl acetate; ketones such as acetone and 2-butanone; nitriles such as acetonitrile; and aprotic polar solvents such as dimethyl sulfoxide, N,N-dimethylformamide and N,N-dimethylacetamide; and water. These solvents may be used alone or in admixture 20 of any.

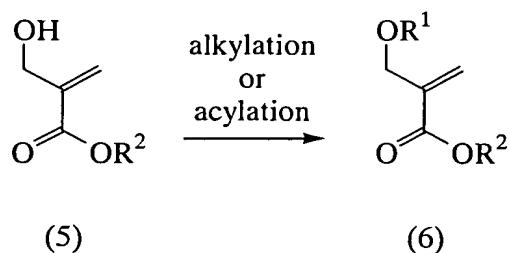
The temperature for the hydroxymethylation is preferably in the range of about -20°C to about 100°C. An appropriate reaction temperature may be selected in the range depending on the reactants and reaction conditions. In an 25 instance where reaction is effected in water using 1,4-diazabicyclo[2.2.2]octane as the amine compound and formaldehyde as the formaldehyde equivalent, a temperature in the range of 0°C to 60°C is preferred. As the reaction temperature raises, more side reactions occur and more 30 formaldehyde is evaporated off. It is thus important for achieving high yields to perform the reaction at a permissible lower temperature within the range where the reaction proceeds at a practically acceptable rate.

For increased yields, the reaction time is desirably 35 determined by monitoring the progress of reaction by thin-layer chromatography (TLC), gas chromatography (GC) or

the like. The reaction time is usually about 1 to about 200 hours.

At the end of reaction, the target compound (5), α -(hydroxymethyl)acrylate compound is recovered by a conventional aqueous workup. The target compound (5) can be purified by any conventional technique such as recrystallization, chromatography or distillation.

10 Next reference is made to the compound of formula (1) wherein R¹ is a C₁-C₁₀ alkyl group which may contain a halogen atom, hydroxyl group, ether bond, carbonyl group, carboxyl group or cyano group. By subjecting the above-obtained α -(hydroxymethyl)acrylate compound of formula (5) to alkylation or acylation in a conventional way, as shown by the reaction scheme below, an target compound of formula (6) 15 can be synthesized. The resulting α -(alkoxymethyl) or α -(acyloxymethyl)acrylate compound of formula (6) can be purified by any conventional technique such as recrystallization, chromatography or distillation.



20 Herein, R^1 is a C_1 - C_{10} alkyl group which may contain a halogen atom, hydroxyl group, ether bond, carbonyl group, carboxyl group or cyano group; and R^2 is a monovalent C_3 - C_{20} organic group having an alicyclic structure.

The inventive alicyclic methacrylate compounds having an oxygen substituent group on their α -methyl group are useful as monomers to form polymers which serve effectively as the base resin in photoresist compositions.

Preparation of a polymer using the inventive alicyclic methacrylate compound as a monomer is generally carried out by mixing the monomer with a solvent, adding a catalyst or

polymerization initiator thereto, and effecting polymerization reaction while heating or cooling if necessary. This polymerization may be done by any conventional technique such as radical, cationic and anionic 5 polymerization techniques. One or more other compounds having a polymerizable double bond can be copolymerized if necessary.

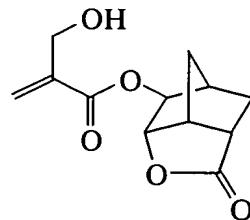
The polymer resulting from the above-described polymerization is used as a base resin to formulate a resist 10 composition. The resist composition is generally formulated by adding an organic solvent and a photoacid generator to the base resin. If necessary, a crosslinking agent, a basic compound, a dissolution inhibitor and the like are further added. Preparation of resist compositions may be done in a 15 conventional way.

EXAMPLE

Examples of the invention are given below by way of illustration and not by way of limitation. In the formulae 20 below, Me is methyl and Ac is acetyl.

Example 1

Synthesis of 2,6-norbornanecarbolacton-5-yl α -(hydroxy-methyl)acrylate



(7)

25

118 g of 2,6-norbornanecarbolacton-5-yl acrylate, 31.8 g of 1,4-diazabicyclo[2.2.2]octane, 50.6 g of 37% formalin and 250 g of tetrahydrofuran were combined and stirred for 20 hours. The reaction solution was neutralized with 30 hydrochloric acid, followed by conventional aqueous workup.

The solvent was distilled off in *vacuo*, after which the product was purified by silica gel chromatography, obtaining 81.0 g (yield 60%) of 2,6-norbornanecarbolacton-5-yl α -(hydroxymethyl)acrylate represented by formula (7).

5 Results of IR and NMR analyses

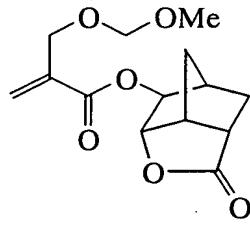
IR (thin film): ν = 3479, 2980, 2883, 1782, 1716, 1637, 1452, 1396, 1342, 1308, 1267, 1180, 1163, 1151, 1057, 1043, 1028, 1012, 998, 954 cm^{-1}

$^1\text{H-NMR}$ (600 MHz in CDCl_3): δ = 1.58 (1H, br. d, J = 11.6 Hz), 1.69 (1H, br. d, J = 13.8 Hz), 1.93 (1H, br. d, J = 11.6 Hz), 1.97 (1H, ddd, J = 13.7, 11.3, 4.5 Hz), 2.24 (1H, br. s), 2.46-2.52 (2H, m), 3.14 (1H, m), 4.23 (2H, s), 4.49 (1H, d, J = 4.8 Hz), 4.58 (1H, m), 5.81 (1H, d, J = 1.0 Hz), 6.15 (1H, d, J = 1.0 Hz)

15

Example 2

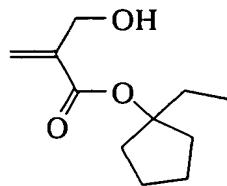
Synthesis of 2,6-norbornanecarbolacton-5-yl α -(methoxymethoxymethyl)acrylate



With stirring, 9.7 g of chloromethyl methyl ether was 20 added to a mixture of 23.8 g of 2,6-norbornanecarbolacton-5-yl α -(hydroxymethyl)acrylate obtained in Example 1, 15.2 g of triethylamine and 200 g of acetonitrile. After 20 hours of stirring, water was added to the reaction solution to stop the reaction. This was followed by conventional aqueous workup. The solvent was distilled off in *vacuo*, after which 25 the product was purified by silica gel chromatography, obtaining 22.0 g (yield 78%) of 2,6-norbornanecarbolacton-5-yl α -(methoxymethoxymethyl)acrylate represented by formula (8).

Example 3

Synthesis of 1-ethylcyclopentyl α -(hydroxymethyl)acrylate



(9)

Reaction was performed as in Example 1 except that
5 95.4 g of 1-ethylcyclopentyl acrylate was used instead of
2,6-norbornanecarbolacton-5-yl acrylate. Purification by
vacuum distillation (boiling point 82°C/30 Pa) gave
10 1-ethylcyclopentyl α -(hydroxymethyl)acrylate represented by
formula (9). The yield was 68%.

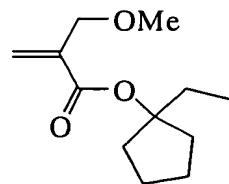
10 Results of IR and NMR analyses

IR (thin film): ν = 3466, 2970, 2877, 1707, 1635, 1462, 1392,
1336, 1273, 1227, 1163, 1113, 1055, 949 cm^{-1}

$^{1}\text{H-NMR}$ (600 MHz in CDCl_3): δ = 0.86 (3H, m), 1.56-1.76 (6H,
m), 2.01 (2H, m), 2.14 (2H, m), 2.61 (1H, br), 4.28 (2H,
15 s), 5.74 (1H, m), 6.16 (1H, m)

Example 4

Synthesis of 1-ethylcyclopentyl α -(methoxymethyl)acrylate



(10)

20 A mixture of 19.8 g of 1-ethylcyclopentyl
 α -(hydroxymethyl)acrylate, 40.0 g of methyl iodide, 30.0 g of
silver (I) oxide and 50 g of N,N-dimethylformamide was

stirred at 50°C for 30 hours. The solids were filtered off, followed by conventional aqueous workup. The solvent was distilled off in vacuo. Purification by distillation (boiling point 53°C/16 Pa) gave 1-ethylcyclopentyl 5 α -(methoxymethyl)acrylate represented by formula (10). The yield was 62%.

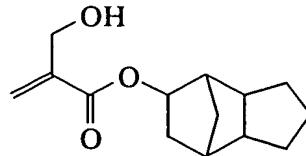
Results of IR and NMR analyses

IR (thin film): ν = 2970, 1939, 2877, 2835, 2816, 1720, 1709, 1637, 1460, 1396, 1323, 1277, 1161, 1113, 948 cm^{-1}

10 $^1\text{H-NMR}$ (600 MHz in CDCl_3): δ = 0.86 (3H, t, J = 7.6 Hz), 1.58-1.75 (6H, m), 2.00 (2H, q, J = 7.6 Hz), 2.14 (2H, m), 3.38 (3H, s), 4.09 (2H, dd), 5.76 (1H, dt), 6.20 (1H, dt)

15 Example 5

Synthesis of 8-tricyclo[5.2.1.0^{2,6}]decyl α -(hydroxymethyl)-acrylate



(11)

20 The procedure of Example 1 was repeated except that 117 g of 8-tricyclo[5.2.1.0^{2,6}]decyl acrylate was used instead of 2,6-norbornanecarbolacton-5-yl acrylate. There was obtained 8-tricyclo[5.2.1.0^{2,6}]decyl α -(hydroxymethyl)acrylate represented by formula (11). The yield was 60%.

Results of IR and NMR analyses

25 IR (thin film): ν = 3467, 2949, 2862, 1709, 1635, 1475, 1448, 1396, 1309, 1267, 1223, 1157, 1134, 1055, 1022, 984, 947 cm^{-1}

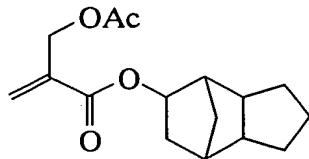
$^1\text{H-NMR}$ (600 MHz in CDCl_3): δ = 0.88-1.00 (2H, m), 1.22 (1H, dt, J = 12.4, 12.4, 6.9 Hz), 1.29 (1H, m), 1.36 (1H,

m), 1.45 (1H, ddd, $J = 13.4, 4.5, 2.1$ Hz), 1.63-1.72 (2H, m), 1.73-1.90 (4H, m), 2.04 (1H, d, $J = 4.5$ Hz), 2.11 (1H, s), 2.40 (1H, br. s), 4.30 (2H, s), 4.65 (1H, $J = 7.2$ Hz), 5.78 (1H, m), 6.19 (1H, d, $J = 1.0$ Hz)

5

Example 6

Synthesis of 8-tricyclo[5.2.1.0^{2,6}]decyl α -(acetoxyethyl)-acrylate



(12)

10 To a mixture of 23.6 g of 8-tricyclo[5.2.1.0^{2,6}]decyl α -(hydroxymethyl)acrylate and 15.8 g of pyridine was added 15.3 g of acetic anhydride. The mixture was stirred for 20 hours. Water was added to the reaction solution to stop the reaction, followed by conventional aqueous workup. The 15 solvent was distilled off in vacuo. Purification by distillation (boiling point 123° C/13 Pa) gave 23.7 g (yield 90%) of 8-tricyclo[5.2.1.0^{2,6}]decyl α -(acetoxyethyl)acrylate represented by formula (12).

Results of IR and NMR analyses

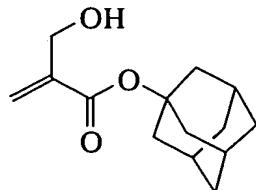
20 IR (thin film): $\nu = 2951, 2864, 1749, 1722, 1643, 1475, 1448, 1400, 1369, 1311, 1271, 1228, 1184, 1167, 1157, 1134, 1047, 982, 953$ cm^{-1}

¹H-NMR (600 MHz in CDCl_3): $\delta = 0.88-0.99$ (2H, m), 1.21 (1H, dt, $J = 12.4, 12.4, 6.5$ Hz), 1.28 (1H, dt, $J = 10.3, 1.2$ Hz), 1.35 (1H, br. d, $J = 10.3$ Hz), 1.44 (1H, ddd, $J = 13.4, 4.5, 2.1$ Hz), 1.62-1.70 (2H, m), 1.72-1.89 (4H, m), 2.03 (1H, d, $J = 4.5$ Hz), 2.08 (3H, s), 2.11 (1H, br. s), 4.65 (1H, br. d, $J = 6.9$ Hz), 4.77 (2H, br. s), 5.78 (1H, m), 6.31 (1H, d, $J = 1.0$ Hz)

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Example 7

Synthesis of 1-adamantyl α -(hydroxymethyl)acrylate

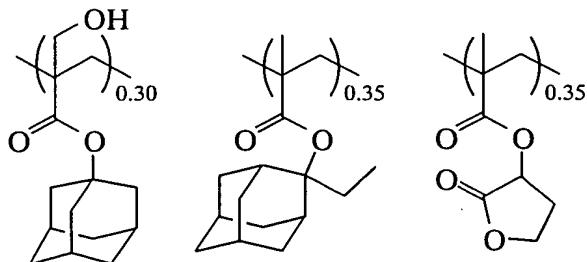


(13)

The procedure of Example 1 was repeated except that
5 117 g of 1-adamantyl acrylate was used instead of
2,6-norbornanecarbolacton-5-yl acrylate. There was obtained
1-adamantyl α -(hydroxymethyl)acrylate represented by formula
10 (13) (yield 60%).

Reference Example 1

Synthesis of a polymer using inventive α -(oxymethyl)acrylic acid ester



(14)

In a nitrogen atmosphere, a mixture of 7.1 g of
15 1-adamantyl α -(hydroxymethyl)acrylate obtained in Example 7,
8.7 g of 2-ethyl-2-adamantyl methacrylate, 6.0 g of
2-oxotetrahydrofuran-3-yl methacrylate, 60 mg of
N,N'-azobisisobutyronitrile, and 80 ml of tetrahydrofuran was
heated and stirred at 60°C for 20 hours. After cooling, the
20 reaction mixture was added dropwise to 2 liters of methanol
under vigorous stirring. The precipitate which settled down
was collected by filtration. The solids were washed with

methanol and dried in vacuo, obtaining 16.4 g of the target polymer of formula (14). The yield was 75%. An component ratio calculated from its ¹H-NMR spectrum indicated a copolymerization ratio of approximately 30:35:35. GPC analysis using polystyrene standards indicated a weight average molecular weight (Mw) of 9,800 and a polydispersity index (Mw/Mn) of 1.80.

Reference Example 2

10 Resist pattern formation using polymer

Using the polymer obtained in Reference Example 1, a resist material was prepared. Its composition was:

(A) 80 parts by weight of the polymer of Reference Example 1 as a base polymer,

15 (B) 1.0 part by weight of triphenylsulfonium trifluoromethanesulfonate as a photoacid generator,
(C) 480 parts by weight of propylene glycol monomethyl ether acetate as a solvent, and
(D) 0.08 part by weight of tributylamine as a basic compound.

20 This was passed through a Teflon® filter having a pore diameter of 0.2 μm. The resist solution was spin coated on a silicon wafer having hexamethyldisilazane sprayed thereon at 90°C for 40 seconds and heat treated at 120°C for 90 seconds, forming a resist film of 500 nm thick. The resist film was
25 exposed to ArF excimer laser light, heat treated at 120°C for 90 seconds, cooled down to 23°C, and dipped in a 2.38% tetramethylammonium hydroxide aqueous solution at 23°C for 60 seconds for development, thereby forming a 1:1 line-and-space pattern. The wafer as developed was observed under top-down
30 SEM. Patterns down to a line width of 0.13 μm existed without collapse or stripping and hence, resolved. This demonstrates that the photoresist material of the invention has improved resolution.

Reference Example 3

Transparency of polymer

The polymer obtained in Reference Example 1, 1.0 g, was dissolved in 6.0 g of cyclohexanone, which was passed through a Teflon® filter having a pore diameter of 0.2 μm . The solution was spin coated on a quartz substrate and heat treated at 90°C for 60 seconds, forming a thin film of 500 nm thick. The thin film was measured for transmittance at 193 nm using a UV-visible spectrophotometer, finding a transmittance of 76% per 500 nm of film thickness. This result demonstrates that the polymer according to the invention has a sufficient transparency as the photoresist base polymer for excimer laser photolithography.

Reference Example 4

Etching resistance of polymer

The polymer obtained in Reference Example 1, 2 g, was dissolved in 10 g of cyclohexanone, which was passed through a Teflon® filter having a pore diameter of 0.2 μm . The solution was spin coated on a silicon wafer and heat treated at 90°C for 60 seconds, forming a thin film of 700 nm thick. Using a reactive ion etching apparatus, the thin film was etched with CF₄ gas under conditions: power 100 W, pressure 5 Pa, and gas flow rate 30 ml/min. As a result, the etching rate was 1.10 based on a rate of 1.00 normalized for novolac resist. For comparison purposes, the same test was done on poly(p-hydroxystyrene) used as the base polymer for KrF resist, finding an etching rate of 1.20. These results demonstrate that the polymer according to the invention has a slower etching rate with CF₄ gas, that is, better dry etching resistance.

There have been described alicyclic methacrylate compounds having an oxygen substituent group on their α -methyl group which are very advantageous as monomers to form polymers having improved transparency, especially at the

exposure wavelength of an excimer laser, and improved dry etching resistance. Resist compositions comprising polymers of the inventive monomers are sensitive to high-energy radiation, show a high resolution, allow smooth development and thus lend themselves to micropatterning. The resist compositions are thus suitable as micropatterning material for VLSI fabrication. Accordingly, the inventive alicyclic methacrylate compounds having an oxygen substituent group on their α -methyl group are quite useful as monomers to form base polymers for resist compositions in satisfying both the resolution and etching resistance of resist.

Japanese Patent Application No. 2003-061476 is incorporated herein by reference.

Although some preferred embodiments have been described, many modifications and variations may be made thereto in light of the above teachings. It is therefore to be understood that the invention may be practiced otherwise than as specifically described without departing from the scope of the appended claims.